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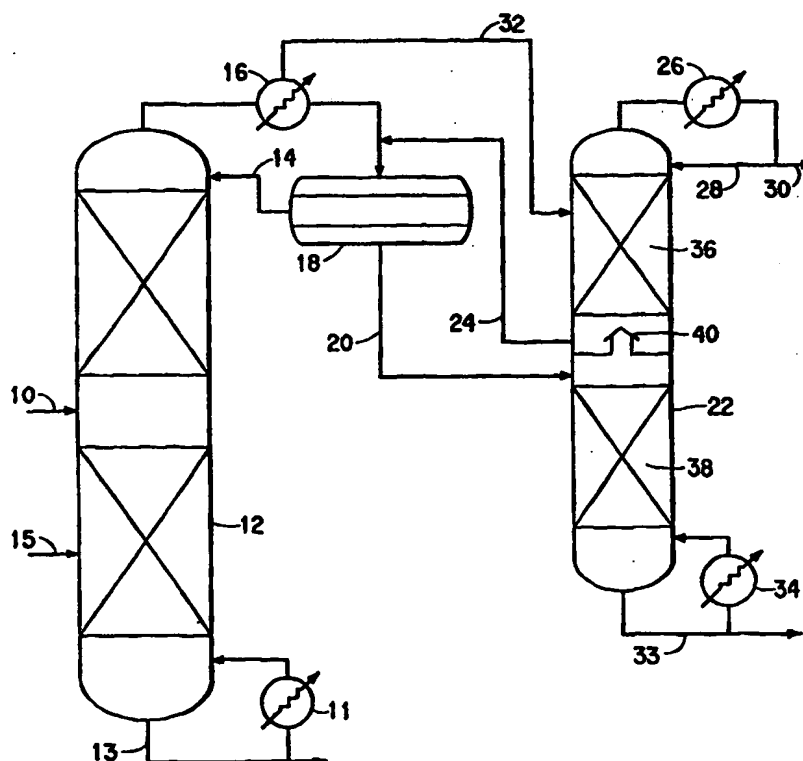
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**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*(54) Title: **WATER SEPARATION PROCESS**

## (57) Abstract

An improved process for azeotropic distillation of a feedstock in which the feedstock comprises an aliphatic carboxylic acid, water and an ester impurity derived from said aliphatic carboxylic acid, wherein the improvement comprises: (a) conducting the azeotropic distillation in the presence of an organic entrainer to produce a liquid phase component comprising said aliphatic carboxylic acid having a reduced water content relative to the water content in the feedstock and a vapor phase component which contains the organic entrainer, water and said ester impurity; (b) condensing the vapor phase component under conditions whereby the organic entrainer and water condense and a substantial portion of the ester impurity remains in the vapor phase; (c) recovering the ester impurity in the vapor phase; (d) separating the organic entrainer and water condensate from step (b) into an organic phase and an aqueous phase; and (e) returning the organic phase to the distillation column.



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**TITLE****WATER SEPARATION PROCESS**

This application claims benefit of GB  
Provisional Application No. 9707177.3, filed April 9,  
5 1997 and U.S. Provisional Application Serial No.  
60/043,841, filed April 11, 1997.

**BACKGROUND OF THE INVENTION**

This invention relates to the separation of  
water from a liquid phase medium containing water and  
10 at least one organic component, e.g. the separation of  
water from an aqueous feed stream containing an  
aliphatic carboxylic acid, such as acetic acid.

In the production of terephthalic acid, for  
example, by the liquid phase oxidation of p-xylene in a  
15 solvent such as acetic acid, water and solvent are  
typically removed as an overhead vapor stream from the  
oxidation reactor as one means for controlling the heat  
of reaction. The vapor stream so removed can contain  
other components, such as, for example, gases (e.g.  
20 unreacted oxygen, carbon oxides and nitrogen) and  
organic components, such as xylene and methyl acetate,  
some of which are formed as a by-product of the  
reaction resulting from oxidation of the acetic acid  
solvent. The vapor stream is condensed to recover  
25 condensibles, some of which may be recycled as reflux  
to the oxidation reactor while other of the  
condensibles are passed to a separation process which,  
in turn, allows for recovery of acetic acid having a  
reduced water content. The feed stream to the  
30 separation process tends to contain methyl acetate  
along with acetic acid and water.

There are a number of options available for  
the handling of the methyl acetate that is recovered  
from the separation process. It may be recycled back  
35 to the reactor where it is believed to suppress  
oxidation of the acetic acid solvent. It may be  
hydrolyzed to methanol and acetic acid which may be  
recycled to the oxidation reactor, or the methyl

acetate may be recovered to use as a fuel or for some other chemical utility.

One convenient form of separation process comprises azeotropic distillation which is preferred over fractional distillation because of its improved energy efficient in operation. However, the presence of methyl acetate in the distillation column tends to interfere with distillation by reducing the amount of the aqueous phase formed from the condensation of the overheads from the column, which, in turn, increases energy consumption and the diameter of the column. With a high enough concentration of methyl acetate in the overheads vapor stream from the distillation column, the vapor phase will tend to condense to a single liquid phase making recovery of water from the overhead product impractical.

The present invention provides a method for managing a low boiling aliphatic carboxylic acid ester impurity, such as methyl acetate, produced as a by-product in the course of producing an aromatic carboxylic acid by liquid phase oxidation of the corresponding precursor in an aliphatic carboxylic acid solvent, especially in circumstances where at least partial recycle of the impurity to the reaction is desirable and where solvent and water from the reaction are to be separated using azeotropic distillation.

#### **SUMMARY OF THE INVENTION**

The present invention provides an improved process for azeotropic distillation of a feedstock in which the feedstock comprises an aliphatic carboxylic acid, water and an ester impurity derived from said carboxylic acid, wherein the improvement comprises:

(a) conducting the azeotropic distillation in the presence of an organic entrainer to produce a liquid phase component comprising said aliphatic carboxylic acid having a reduced water content relative to the water content in the feedstock and a

vapor phase component which contains the entrainer, water and said ester impurity;

(b) condensing the vapor phase component under conditions whereby the organic entrainer and water  
5 condense while a substantial portion of the ester impurity remains in the vapor phase;

(c) recovering the ester impurity in the vapor phase;

(d) separating the organic entrainer and water  
10 into an organic phase and an aqueous phase; and

(e) returning the organic phase to the distillation column.

The azeotropic distillation process is carried out according to the invention using an organic  
15 entrainer which is an ester selected from n-propyl acetate and iso-butyl acetate.

In one embodiment of the invention, the vapor phase component, which comprises the organic entrainer, water and the carboxylic acid ester  
20 impurity, is removed from the distillation process as a tops product, i.e., an overhead vapor stream, from the distillation column.

In an alternative embodiment of the invention, the azeotropic distillation column is  
25 extended, i.e., it can be elongated, so that the vapor phase component comprising the organic entrainer, water and the ester impurity pass into the extended section and undergo further distillation whereby the organic entrainer and water are condensed  
30 and recovered from the column as a liquid phase, and the ester impurity remains in the vapor phase. The recovered organic entrainer/water liquid phase can then be allowed to phase separate into said organic and aqueous phases.

35 According to another aspect, the present invention is an improved process for producing an aromatic carboxylic acid, preferably terephthalic acid, by liquid phase oxidation of a precursor of

said acid, i.e., paraxylene, in an aliphatic acid solvent, i.e., acetic acid, in the presence of a catalyst system, wherein the improvement comprises:

- 5 (a) controlling the heat of reaction by removing from the oxidation reaction an overheads vapor stream which comprises the aliphatic acid solvent, water produced in the reaction and an impurity formed as a by-product of the oxidation reaction which is an ester derivative of the aliphatic acid solvent;
- 10 (b) deriving from the overheads vapor stream a first liquid phase component which contains the aliphatic acid solvent, water and said impurity;
- (c) azeotropically distilling said first liquid phase component in the presence of an organic  
15 entrainer to produce a second liquid phase component comprising said aliphatic carboxylic acid solvent having a reduced water content relative to the water content in the first liquid phase and a vapor phase component which contains the organic entrainer, water  
20 and said impurity;
- (d) condensing the vapor phase component under conditions whereby the organic entrainer and water condense while a substantial portion of the impurity remains in the vapor phase;
- 25 (e) recovering the impurity in the vapor phase;
- (f) separating the organic entrainer and water condensate from step (d) into an organic phase and an aqueous phase;
- (g) returning said organic phase to the  
30 distillation column; and
- (h) returning at least part of said recovered impurity to the oxidation reaction.

The improved process according to the invention makes it economically feasible on a commercial scale to  
35 recycle to the oxidation reactor substantially all of the ester impurity that formed as a by-product during the oxidation reaction and is withdrawn from the reaction zone via an overheads vapor stream and thereby

establish a standing concentration of the ester impurity such that the production of the impurity in the oxidation reactor, i.e., the oxidation reaction zone, is balanced by its destruction. Thus, a substantial level of said impurity can be recycled to the oxidation reactor without suffering a reduction in energy savings otherwise made possible by using azeotropic distillation to separate water from the aliphatic carboxylic acid solvent.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic process diagram which illustrates one embodiment of the invention in which water is separated from acetic acid solvent via azeotropic distillation, and methyl acetate is recycled.

Fig. 2 is a schematic diagram of an alternative embodiment of the invention.

#### DETAILED DESCRIPTION

The present invention is an improved process for producing an aromatic carboxylic acid, particularly terephthalic acid, by liquid phase oxidation of a precursor of the acid, i.e., paraxylene, in an aliphatic acid solvent, i.e., acetic acid, in the presence of a catalyst system, wherein the improvement comprises:

(a) controlling the heat of reaction by removing from the oxidation reaction zone an overheads vapor stream which comprises the aliphatic acid solvent, water produced in the reaction and an impurity formed as a by-product of the oxidation reaction which is an ester derivative of the aliphatic acid solvent;

(b) deriving from the overheads vapor stream a first liquid phase component which contains the aliphatic acid solvent, water and said impurity;

(c) azeotropically distilling said first liquid phase in the presence of an organic entrainer selected from n-propyl acetate and iso-butyl acetate to produce a second liquid phase component comprising

said aliphatic carboxylic acid solvent having a reduced water content relative to the water content in the first liquid phase and a vapor phase component which contains the organic entrainer, water and said  
5 impurity;

(d) condensing the vapor phase component under conditions whereby the organic entrainer and water condense while a substantial portion of the impurity remains in the vapor phase;

10 (e) recovering the impurity in the vapor phase;

(f) separating the organic entrainer and water condensate from step (d) into an organic phase and an aqueous phase;

(g) returning said organic phase to the  
15 distillation column; and

(h) returning at least part of said recovered impurity to the oxidation reaction zone.

The first liquid phase component derived from the overheads vapor stream may be isolated by  
20 condensing a substantial proportion of the condensible components of the overheads stream in one or more stages. Depending on how the process is to be operated, the first liquid phase may comprise a relatively water rich, carboxylic acid lean fraction  
25 (water draw off stream) of the condensate, with a corresponding relatively water lean, carboxylic acid rich fraction. The carboxylic acid rich fraction is recycled as a reflux stream to the oxidation reaction, i.e. reaction zone or oxidation reactor.  
30 In the case where the carboxylic acid rich fraction is recycled as a reflux to the oxidation reaction, it will be understood that part of the ester impurity will necessarily by-pass azeotropic distillation and be returned directly to the oxidation reaction via  
35 the reflux stream. Thus, where reference is made above to recycling all of the impurity to the oxidation reaction, some may be recycled via azeotropic distillation and some via the reflux



stream. In addition, in practice it has been observed that some of the impurity may remain in vapor form following said condensation of the overheads stream. This fraction of the impurity may  
5 be recovered in an absorber and, if desired, also recycled to the oxidation reaction.

The aromatic carboxylic acid production processes in which the instant invention is most applicable are those processes employed on a  
10 commercial scale for production of terephthalic acid and isophthalic acid in which the aliphatic carboxylic acid solvent is typically acetic acid, and the ester impurity formed as a by-product in the oxidation reaction is methyl acetate.

15 In practice, the feedstock supplied to the azeotropic distillation column can also include aqueous feeds derived from other aspects of the process for the aromatic carboxylic acid, such as, for example, the purification step as described in  
20 EP-A-498501, the teachings of which are incorporated herein by reference. Thus, the aromatic carboxylic acid produced by the oxidation reaction referred to above may be dissolved in water to form an aqueous solution and then purified by hydrogenation under  
25 elevated temperature and pressure conditions. Following hydrogenation, the purified aromatic carboxylic acid is separated from the mother liquor, and the mother liquor is supplied to the azeotropic distillation column as such and/or after further  
30 treatment (involving, for instance, precipitation and separation of less pure aromatic carboxylic acid therefrom).

The invention will now be illustrated by the use of examples based on computer simulations with  
35 references to Figs. 1 and 2. Four cases have been examined in which water was separated from acetic acid using normal propyl acetate as the organic entrainer

with varying amounts of methyl acetate present and varying column configurations.

The water draw off and combined feeds to a separations train are summarized in Table 1 and the results from the simulations are summarized in Table 2. Referring to Fig. 1, a feed stream 10 to distillation column 12 (which may be a packed or a tray type column) comprises the water draw off obtained from the oxidation reactor overheads condenser system associated with the oxidation reactor for the production of terephthalic acid. Some condensate remaining after water draw off is typically recycled directly to the reactor. In addition, a further feed stream 15 is shown which is intended to represent combined feeds to the distillation column 12 from other parts of the plant or production process. Heat to column 12 is supplied via reboiler 11. A low boiling point organic entrainer, such as n-propyl acetate, is supplied to the column via line 14, and the column is operated so as to insure penetration of the entrainer to a level below feed 10 whereby feed 10 enters the column at an entrainer-rich region. Feed 15 represents a combination of other possible aqueous feeds (liquid or vapor) that may be introduced to other points along the height of the column either within or below the azeotropic zone. These feeds may be derived from a high pressure absorber and/or a first and second crystallizer which may also be associated with the oxidation reactor or the feeds may come from a purification process. In operation, the primary feed will be the water draw off stream derived from the reactor overheads system which will generally contribute more water than any of the other feeds which may optionally be present. In some cases, such other feeds represented within stream 15 may be combined with feed from the reactor overheads condenser system and introduced into column 12 as a single feed.

The bottoms product withdrawn from the base of column 12 via line 13 comprises acetic acid having a relatively low water content relative to the incoming feed stream 10 and is suitable for recycle to the oxidation reaction. The tops product at the head of column 12 is cooled in a column overheads condenser system 16, and the condensate is supplied to phase separator 18 where condensate is separated into an organic phase (primarily organic entrainer with a small quantity of water and some methyl acetate, paraxylene and other organics) and an aqueous phase containing a small quantity of entrainer and, *inter alia*, some methyl acetate. The organic phase comprising mainly entrainer is reintroduced into the distillation column via line 14 while the aqueous phase is passed via line 20 to a stripping column 22 for recovery of entrainer via line 24 for recycle to the azeotropic distillation column and recovery of methyl acetate as a vapor phase tops product which is condensed in condenser 26. Part of the recovered methyl acetate is refluxed to the stripping column via line 28, and the remainder is recovered via line 30.

In stripping column 22, heat is supplied by reboiler 34, and the column comprises upper and lower packed or trayed sections 36 and 38, respectively, with the aqueous phase from the separator 18 being fed to the column via line 20. A separator device 40 is provided within stripping column 22 which allows upward passage of vapor in column 22 but which also prevents downward passage of the liquid phase. Separator device 40 serves to collect an entrainer rich fraction which is returned via tray 41 and line 24 to the phase separator. Alternatively, the entrainer rich fraction recovered from device 40 may be processed to remove water therefrom (not shown), and the entrainer can then be passed directly into column 12, e.g., via reflux line 14. The bottoms product obtained from the

stripping column comprises water, which is largely free of entrainer, and organics and is removed via line 33.

As thus far described, the scheme of Fig. 1 can cope with feed streams in which the methyl acetate content is low, typically where the methyl acetate content is from 30 to 100 times less than the water content on a weight basis. However, if it is desired to recycle methyl acetate to the oxidation reaction zone, the methyl acetate concentration of the water draw off stream derived from the reactor overheads condenser system (i.e., line 10) will tend to be relatively high (typically in the range from 2% to 10%, but usually 4% to 9%, on a weight basis of the draw off stream) and will be detrimental to efficient, i.e., optimum economical, operation of the azeotropic distillation column. In particular, the amount of aqueous phase from condensation of the overheads phase from column 12 will tend to decrease causing the heat load in the column to increase. Consequently there is a serious disincentive to use azeotropic distillation in circumstances where recycle of methyl acetate to the oxidation reactor is desired. This is illustrated by comparing Case 1 and Case 2 in Table 2 which were modeled with operation as described above.

The problem arising when high concentrations of methyl acetate are present in feed stream 10 is overcome in the full embodiment of Fig. 1 by controlling the condensation step upstream of phase separator 18 to allow for a methyl acetate rich vapor stream to be obtained whereby the amount of methyl acetate routed to phase separator 18 via the condensate can be reduced to manageable levels without materially affecting the efficiency of operation of the azeotropic distillation process. Thus, as shown in Fig. 1, condenser system 16 is operated under conditions whereby a vapor phase side stream 32, which is rich in methyl acetate, is obtained, side stream 32 being supplied directly to stripping column 22 as shown for

recovery of the methyl acetate and entrainer contained in the side stream. The benefit of operating with a vapor side stream 32, from condenser 16 to a stripping column 22 is illustrated via Case 3 in Table 2.

5        Fig. 2 illustrates an alternative embodiment of the invention which is generally similar to Fig. 1 such that like reference numerals are used to identify components which function in the manner described with reference to the embodiment of Fig. 1. In the  
10        embodiment of Fig. 2, column 12 is extended, i.e., elongated, to incorporate section 42 in the upper portion thereof in which a substantial fraction of the methyl acetate is separated as a vapor phase and in which a separator device 44 is installed to collect  
15        entrainer, water and a small amount of methyl acetate as a liquid phase for supply via line 46 to phase separator 18. The overheads vapor stream from section 42 is passed to overheads condenser 48 to condense methyl acetate, and the condensate is, in part,  
20        refluxed via line 50 and, in part, removed for recycle to the oxidation reaction via line 52 as shown.

      Separator 18 serves to separate the liquid phase supplied via line 46 into an organic phase, which is reintroduced via line 54 into column 12 at a point  
25        below the separator device 44 and an aqueous phase which is passed via line 20 to stripping column 22. Compared to the embodiment of Fig. 1, the embodiment of Fig. 2 does not require an overheads condensing system associated with stripping column 22 for recovery of the  
30        methyl acetate. Instead, the vapor phase rich in methyl acetate is recycled via line 56 to column 12 at section 42 of this embodiment, and this has been modeled as Case 4 in Table 2.

Table 1

Case Number and Streams	Acetic Acid Flow kg/hr	Water Flow kg/hr	Methyl Acetate Flow kg/hr
Water Draw Off - 1	57,115	20,762	360
Water Draw Off - 2	57,115	20,762	1983
Water Draw Off - 3	57,115	20,762	1983
Water Draw Off - 4	57,115	20,762	1983
Combined Feeds - 1	117,158	28,789	440
Combined Feeds - 2	117,158	28,789	2357
Combined Feeds - 3	117,158	28,789	2357
Combined Feeds - 4	117,158	28,789	2357

Table 2

5

	Case 1	Case 2	Case 3	Case 4
Combined Heat load (MW)	22.15	34.2	23.01	21.83
Methyl Acetate Recovered (kg/hr)	421	2347	2335	2336
Methyl Acetate Percent of Organic Phase from Decanter	6.9	32.4	6.3	1.5
Water Percent of Organic Phase from Decanter	3.4	3.6	3.4	3.4
Percent Aqueous Phase from Decanter	13.34	10.92	14.09	13.12

**WHAT IS CLAIMED IS:**

1. An improved process for azeotropic  
5 distillation of a feedstock in which the feedstock  
comprises an aliphatic carboxylic acid, water and an  
ester impurity derived from said aliphatic carboxylic  
acid, wherein the improvement comprises:
  - (a) conducting the azeotropic distillation in  
10 the presence of an organic entrainer to produce a  
liquid phase component comprising said aliphatic  
carboxylic acid having a reduced water content  
relative to the water content in the feedstock and a  
vapor phase component which contains the organic  
15 entrainer, water and said ester impurity;
  - (b) condensing the vapor phase component under  
conditions whereby the organic entrainer and water  
condense and a substantial portion of the ester  
impurity remains in the vapor phase;
  - 20 (c) recovering the ester impurity in the vapor  
phase;
  - (d) separating the organic entrainer and water  
condensate from step (b) into an organic phase and an  
aqueous phase; and
  - 25 (e) returning the organic phase to the  
distillation column.
2. The improved distillation process of Claim 1  
in which the organic entrainer is an ester selected  
from n-propyl acetate and iso-butyl acetate.
- 30 3. The improved distillation process of Claim 1  
comprising the additional steps of (i) removing the  
vapor phase component of step (a) from the distillation  
process; (ii) condensing it to form an organic phase  
and an aqueous phase; (iii) recycling the organic phase  
35 to the distillation process; (iv) stripping the aqueous  
phase to recover organic entrainer and form a second  
vapor phase containing said ester impurity.

4. The improved distillation process of Claim 3 comprising the additional steps of (v) condensing the second vapor phase; and (vi) recycling at least some of the condensate from step (v) to said stripping step (iv).

5. An improved process for producing an aromatic carboxylic acid by liquid phase oxidation of a precursor of said acid in an aliphatic acid solvent in the presence of a catalyst system, wherein the improvement comprises:

(a) removing from the oxidation reaction an overheads vapor stream which comprises the aliphatic acid solvent, water produced in the reaction and an impurity formed as a by-product of the oxidation reaction which is an ester derivative of the aliphatic acid solvent;

(b) deriving from the overheads vapor stream a first liquid phase component which contains the aliphatic acid solvent, water and said ester impurity;

(c) azeotropically distilling said first liquid phase component in the presence of an organic entrainer to produce a second liquid phase component comprising said aliphatic carboxylic acid solvent having a reduced water content relative to the water content in the first liquid phase and a vapor phase component which contains the organic entrainer, water and said ester impurity;

(d) condensing the vapor phase component under conditions whereby the organic entrainer and water condense while a substantial portion of the ester impurity remains in the vapor phase;

(e) recovering said ester impurity in the vapor phase;

(f) separating the organic entrainer and water condensate from step (d) into an organic phase and an aqueous phase;



(g) returning said organic phase to the distillation column; and

(h) returning at least part of said recovered ester impurity to the liquid phase oxidation reaction.

5        6. The improved process of Claim 6 in which the aromatic carboxylic acid is terephthalic acid, the precursor of said acid is paraxylene, the aliphatic acid solvent is acetic acid, the impurity formed as a by-product is methyl acetate, and the organic entrainer  
10 is selected from n-propyl acetate and iso-butyl acetate.

1/2

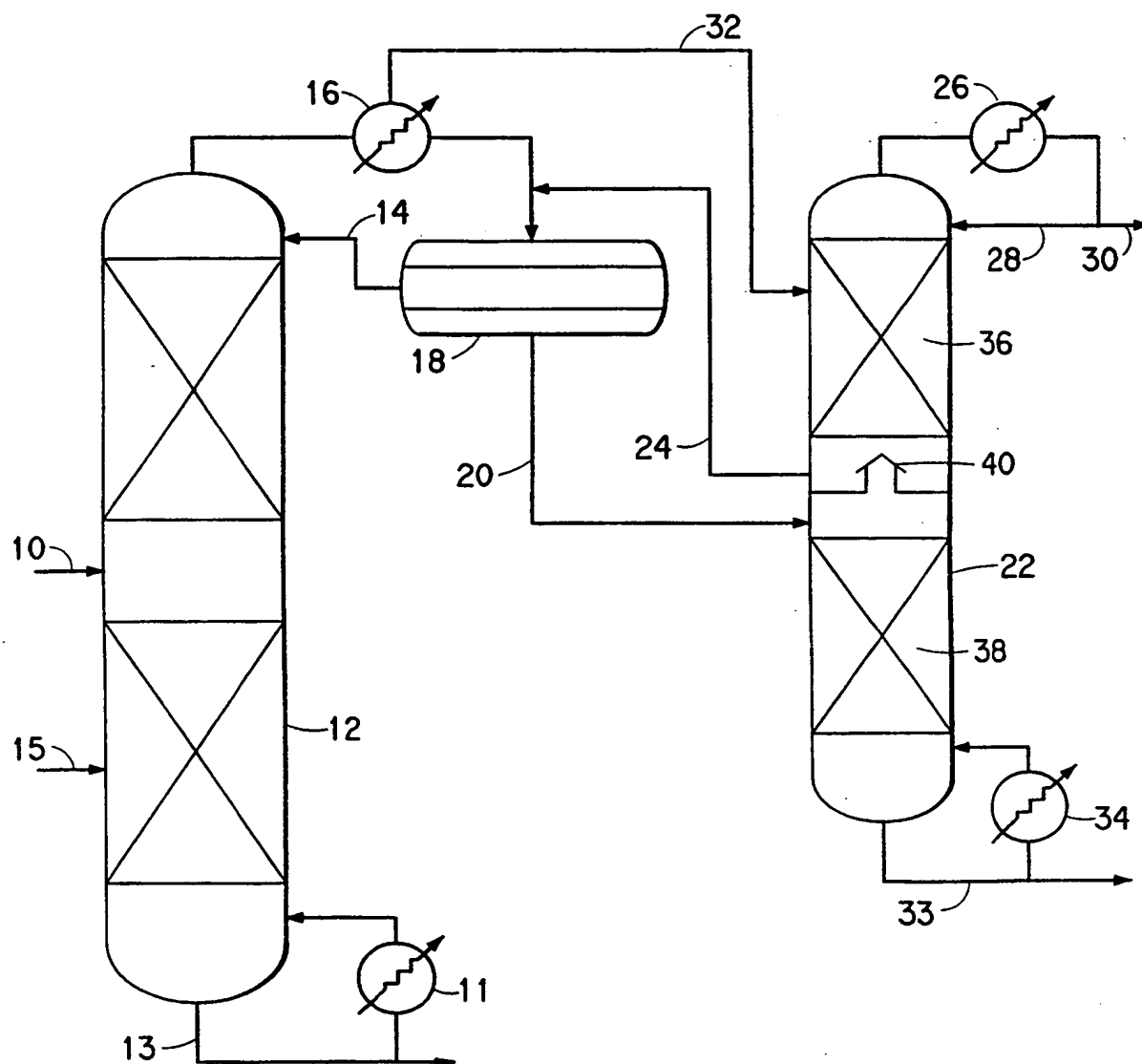


FIG. 1

2/2

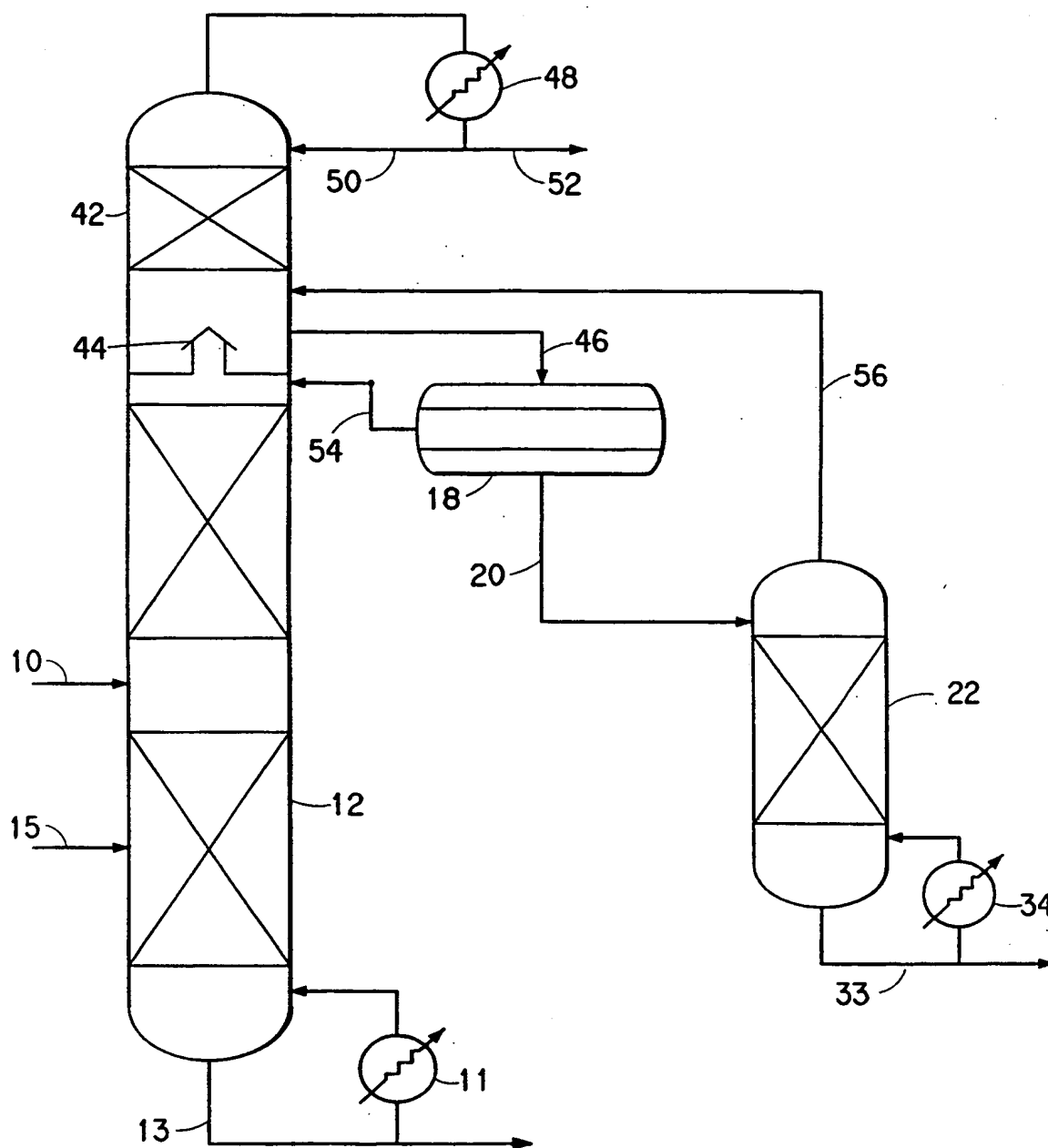


FIG. 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/06740

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07C51/46 C07C53/08

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 06065 A (ICI PLC ;PARTEN WILLIAM DAVID (GB); URE ALAN MACPHERSON (GB)) 29 February 1996 see page 7, line 13 - line 27 see page 8, line 30 - page 9, line 4 see claims 1,14	1,2,5,6
A	US 4 250 330 A (COSTANTINI GIUSEPPE ET AL) 10 February 1981 see column 2, line 43 - line 59 see example 1 see claim 1	1,5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/06740

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 273 744 A (SOCIÉTÉ ANONYME DES DISTILLERIS DES DEUX-SÈVRES) 1 November 1928 see page 1, line 61 - line 89 see example 1 see claim 1	1
P.X	WO 97 29068 A (ICI PLC ;PARTEN WILLIAM DAVID (GB)) 14 August 1997 see page 4, line 23 - page 5, line 3 see page 8, line 28 - page 9, line 4 see example see claims 1-4,7-12	1,2,5,6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

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